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# STUDY OF IRRADIATION-INDUCED ACTIVE SITES ON MAGNESIUM OXIDE WITH THE USE OF ELECTRON PARAMAGNETIC RESONANCE

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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# STUDY OF IRRADIATION-INDUCED ACTIVE SITES ON MAGNESIUM OXIDE

## WITH THE USE OF ELECTRON PARAMAGNETIC RESONANCE\*

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Lewis Research Center

### SUMMARY

The ultraviolet-irradiation-induced catalytic activity of magnesium oxide and the electron paramagnetic resonance spectra on the same sample were studied. The data show that a correlation exists between the  $V_1$  center concentration and the enhanced catalytic activity for the hydrogen-deuterium exchange reaction,  $H_2 + D_2 \rightleftharpoons 2HD$ . (The  $V_1$  center is defined as a hole trapped at an anion adjacent to a cation vacancy.) Samples were subjected to (a) degassing at 290° and 500° C, (b) thermal decay at -79°, 0°, and 30° C, (c) 2537 Å ultraviolet light as a function of time, and (d) several different wavelengths of ultraviolet light. It is concluded that either a  $V_1$ -type center existing on the surface is an active site for the exchange reaction or the  $V_1$  center formation is an integral step in the formation of the active site; that is, it is a hole trap that prevents recombination.

### INTRODUCTION

A previous investigation (ref. 1) showed that the catalytic activity of magnesium oxide (MgO) powders for the hydrogen-deuterium exchange reaction,  $H_2 + D_2 \rightleftharpoons 2HD$ , can be enhanced by ultraviolet irradiation provided that the catalyst is not completely degassed. The present investigation is a study of the induced catalytic activity and electron paramagnetic resonance spectra on the same sample. Magnesium oxide catalysts are particularly suitable for such studies since the electron paramagnetic resonance spectra of MgO single crystals have been extensively explored by Wertz and coworkers (refs. 2 to 4).

The role of unpaired electrons in adsorption on metals has been elucidated by the work of Selwood (ref. 5) and others, who used magnetization techniques. Kohn (ref. 6) observed the interaction between paramagnetic centers in silica gel and adsorbed gases, while Kokes (ref. 7) made a similar study on zinc oxide. It follows that some such centers may act as catalytic sites. From a comparison of electron paramagnetic resonance data on irradiated single crystals, it was suggested in reference 1 that the active site following irradiation was the ferric ion  $Fe^{+3}$ , which was present as an impurity. The present investigation showed that the  $Fe^{+3}$  concentration actually decreased upon irradiation.

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ation for the powders of catalytic interest. Subsequent data in this report show, however, that a correlation does exist between the  $V_1$  center concentration and the irradiation-induced catalytic activity.

The  $V_1$  center is defined in figure 1 as a hole trapped at an anion adjacent to a cation vacancy. Several conditions must be satisfied for the for-

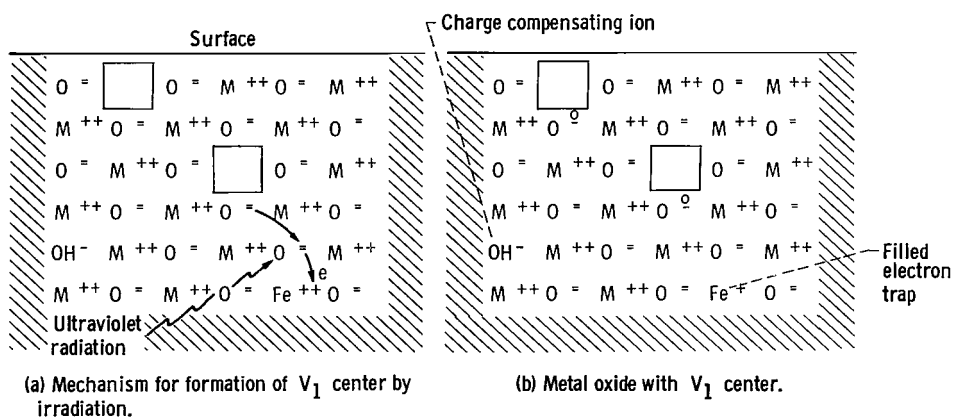


Figure 1. - Metal-oxide lattice with  $V_1$  center, electron trap, and charge compensating ion.

mation of a  $V_1$  center: (a) charge compensation for the cation vacancy, (b) quanta of light with sufficient energy to free an electron, and (c) an electron trap. Irradiation removes electrons from the valence band, and the resulting electron hole (called simply a hole) is then free to move through the lattice until it is trapped at the cation vacancy. This center now has an unpaired electron that may be detected by electron paramagnetic resonance techniques.

## EXPERIMENTAL

The catalysts used in this investigation were prepared from reagent-grade  $MgO$ . Most of the experiments were carried out on pellets that were made from a paste of the powder and distilled water. These pellets, called P-1 in this report, were dried in air at  $100^\circ C$  and evacuated at  $290 \pm 5^\circ C$  or  $500 \pm 5^\circ C$ . Some data were obtained on the original powder, P-2, after evacuation at the elevated temperatures. A third sample, P-3, was doped by impregnation with 35 parts per million iron and fired at  $800^\circ C$  in vacuum.

Batch reactions were carried out in fused quartz reactors with a volume of about 10 cubic centimeters. The pressure of the reacting mixture was 20 millimeters of mercury. All rate measurements reported in this report were carried out at  $-78^\circ C$  and are expressed by a first-order rate constant. The gas samples were analyzed for percent HD with a mass spectrometer.

The ultraviolet lamps were of (a) a hot-cathode-type, mercury-argon discharge tube with the inner wall coated with a conversion phosphor with its output in the range of 3100 to 4000 Å and (b) a hot-cathode-type tube with peak output at 2537 Å. The longer wavelength lamp was used in conjunction with a

filter that removed the 3125 Å lines from the spectrum. All irradiations were carried out at  $23 \pm 3^\circ \text{C}$ .

The electron paramagnetic resonance spectrometer used for this investigation was equipped with a 100-kilocycle modulation unit. The cavity resonance frequency was about 9500 megacycles per second. Measurements were made near  $77^\circ \text{K}$  by passing dry nitrogen gas through a liquid-nitrogen heat exchanger and then past the sample.

### ELECTRON PARAMAGNETIC RESONANCE SPECTRUM

If the trapped hole in figure 1 is localized upon one oxygen ion for a time that is long compared with  $10^{-7}$  second, then the defect shows axial-electric-field symmetry with the principal axis of the crystal as symmetry axis (ref. 4). Wertz (ref. 4) observed the spectrum of the  $V_L$  center, which can be described by  $g_{\parallel} = 2.0032$  (magnetic field along the symmetry axis) and  $g_{\perp} = 2.0385$  (magnetic field perpendicular to the symmetry axis), where  $g$  is the spectroscopic splitting factor. The lines broaden at temperatures higher than  $77^\circ \text{K}$  and cannot be observed after the irradiated sample has been heated to  $100^\circ \text{C}$  for a few minutes.

The shape of the paramagnetic resonance absorption curve for such a center in a polycrystalline sample is treated elsewhere (refs. 8 and 9). For  $g_{\perp} > g_{\parallel}$  the derivative of the absorption curve will show a maximum at  $g_{\perp}$  and a minimum at  $g_{\parallel}$ .

The derivative spectrum of P-1 after ultraviolet irradiation at 2537 Å is shown in figure 2. Arrows depict the  $g$ -components reported in reference 4. A symmetric line is slightly to the low-field side of the  $g_{\parallel}$  minimum. In addition to the similarity of  $g$ -values to those reported in reference 4, the relaxation times for the irradiation-induced center were so short that the spectrum could be observed only near  $77^\circ \text{K}$ ; hence, it may be concluded that the  $V_L$  center was being observed in the catalyst sample. The line at the higher field was due to the chromium ion  $\text{Cr}^{+3}$ , which was saturated with microwave power.

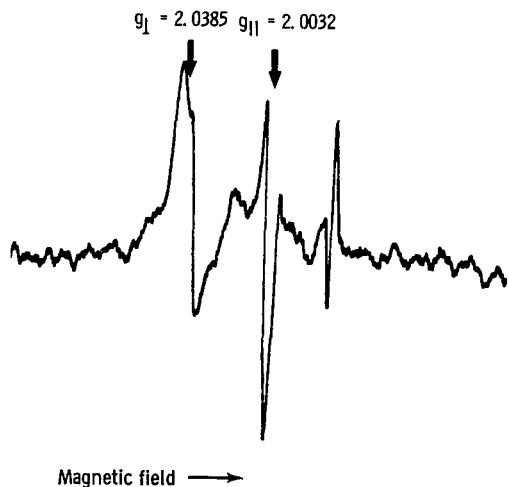


Figure 2 - Spin resonance curve of magnesium oxide catalyst degassed at  $290^\circ \text{C}$  in vacuum and irradiated with 2537 Å ultraviolet light.

At present, it is not clear whether there is any contribution to the spectrum from  $V_L$ -type centers existing on the surface. By definition the  $V_L$  center cannot be a surface defect; however, a hole-trapping center at the surface, as shown in figure 1, may have an electron paramagnetic resonance spectrum that is quite similar to the  $V_L$  center in the bulk. Experimental evidence is not conclusive. At a pressure of about 20 mil-

limeters of mercury and a temperature of  $-78^{\circ}\text{C}$ , hydrogen ( $\text{H}_2$ ), oxygen ( $\text{O}_2$ ), or carbon dioxide ( $\text{CO}_2$ ) had little or no effect on the spectrum shown in figure 2. On the iron-doped sample P-3,  $\text{H}_2$  and  $\text{O}_2$  destroyed the  $V_1$  center spectrum in a few seconds. The  $V_1$  centers were apparently formed in the iron-doped sample degassed at  $800^{\circ}\text{C}$  because  $\text{Fe}^{+5}$  ions acted as charge-compensating centers for the magnesium ion vacancy.

## RESPONSE OF $V_1$ CENTER CONCENTRATION AND CATALYTIC ACTIVITY TO VARIOUS TREATMENTS

In an attempt to show that the enhanced catalytic activity is related to the  $V_1$  center concentration, the samples were subjected to the following treatments: (a) degassing at  $290^{\circ}\text{C}$  and  $500^{\circ}\text{C}$ , (b) thermal decay at  $-79^{\circ}$ ,  $0^{\circ}$ , and  $30^{\circ}\text{C}$ , (c) irradiation with 2537 Å ultraviolet light as a function of time, and (d) irradiation with several different wavelengths of ultraviolet light. Unless otherwise indicated, these treatments were carried out on P-1.

When the samples were degassed at  $290^{\circ}\text{C}$  and then irradiated with 2537 Å ultraviolet light, the catalytic activity increased about tenfold over the unirradiated samples, and the  $V_1$  center spectrum appeared. The catalytic activity of the samples degassed at  $500^{\circ}\text{C}$  and irradiated showed no change in activity and no  $V_1$  center spectrum. The effect of degassing at  $290^{\circ}\text{C}$  is the partial removal of surface and interlattice hydroxyl groups. The remaining hydroxyl ions probably act as charge-compensating centers for the cation vacancies. Their role as electron acceptors during irradiation is also possible. When these hydroxyl groups are removed by degassing at higher temperatures, the cation vacancies are no longer stable.

The decay in catalytic activity and  $V_1$  center concentration was followed at three temperatures following 2537 Å ultraviolet irradiation. The

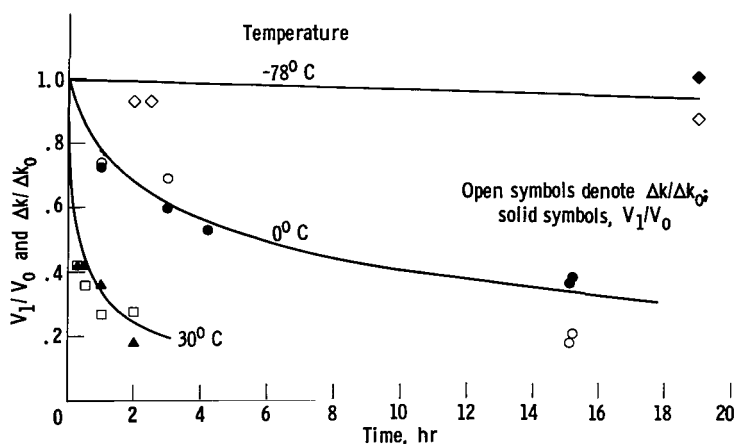


Figure 3. - Thermal decay at three temperatures following 2537 Å ultraviolet irradiation. Curves at  $0^{\circ}$  and  $30^{\circ}\text{C}$  represent equation (3) with constants  $C_1$  and  $C_2$  fitted to experimental points.

sample had been degassed at  $290^{\circ}\text{C}$  and in most cases the catalytic and electron paramagnetic resonance measurements were made successively. In order to prevent bleaching with room lights, the samples were kept in partial darkness. Results of these thermal decay experiments are shown by the points in figure 3, where  $\Delta k$  is the difference in rate constants before and after irradiation, while  $\Delta k_0$  and  $V_0$  are the enhanced rate constant and the  $V_1$  center concentration immediately after irradiation, respectively.

Response of the catalytic activity and  $V_1$  center concentration to 2537 Å ultraviolet irradiation is shown in figure 4. In this case the sample was irradiated for 0.5, 4.5, and 45 minutes with the electron paramagnetic resonance spectrum recorded after each irradiation interval. The catalyst was then heated to 200° C to remove any effects of the first ultraviolet treatment. The catalytic activity was measured after the same intervals of irradiation. While some scatter exists in the data, more than half of the change took place in the first 30 seconds of irradiation.

Various wavelengths of light were used for irradiation to determine qualitatively the threshold energy for the formation of the  $V_1$  center and the enhanced activity. The intensities of the various portions of the spectra were not necessarily the same. The data show that a wavelength of light of less than 3200 Å is required to form the  $V_1$  center and the active site. The cut-off wavelength seems to be about 3100 Å or 4 electron volts. This observation confirms earlier work (ref. 10), which showed that a Pyrex reactor that acts as a filter of 50 percent efficiency for 3100 Å light reduces the enhanced catalytic activity considerably.

Catalyst P-2, which can be compared with that used in reference 1, was subjected to similar tests, and qualitatively the agreement between catalytic activity and  $V_1$  center concentration was substantiated. For this powder, however, a considerable error was introduced into the measurements since the  $V_1$  center line was not more than five times the noise level. The preirradiation activation energy at -78° C for the exchange reaction was 5 and 0.6 kilocalorie per gram-mole for P-2 and P-1, respectively. The same response to irradiation for different catalysts would not necessarily be expected.

## DISCUSSION OF RESULTS

Perhaps the strongest evidence that the active site for catalysis is closely related to the  $V_1$ -type center comes from the thermal decay data. A decay scheme has been proposed for MgO single crystals by Soshea, Dekker, and Sturtz (ref. 11) that can be adapted to the present experiment. Irradiation with ultraviolet light presumably produces a number of trapped electrons and

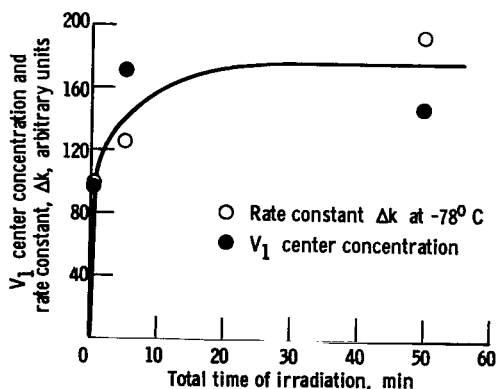


Figure 4. - Response of catalytic activity and  $V_1$  center concentration to 2537 Å ultraviolet irradiation at 23° C.

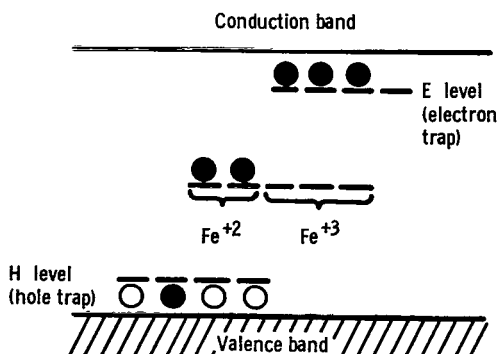


Figure 5. - Schematic energy-level diagram for irradiated magnesium oxide. (After ref. 11).

holes with a resulting band scheme as shown in figure 5. At a given temperature the electrons trapped at E levels or holes at H levels ( $V_1$  centers) will be released thermally.

Let  $N$  be the total number of E levels and let  $n(t)$  of them be occupied by electrons. The probability for an electron thermally released from an E level to combine with a trapped hole is  $p$ ; the probability for this electron to return to an E level is then  $1 - p$ , where

$$p = \frac{\alpha n}{\alpha n + \beta(N - n)} \quad (1)$$

In this equation,  $\alpha$  is the cross section for the trapping of an electron by a  $V_1$  center and  $\beta$  is the same quantity for an E level. Equation (1) implies that the cross sections  $\alpha$  and  $\beta$  are large compared with those of other electron sinks. Experiments on the catalysts indicate that this is the case for temperatures less than  $100^\circ \text{C}$ . The rate of decay of electrons will therefore be equal to the rate of decay of  $V$  centers. This decay is determined by

$$\frac{dn}{dt} = -\gamma p n \quad (2)$$

where  $\gamma$  is a proportionality constant depending on temperature. The solution of the equation obtained by substituting (1) into (2) may be written as

$$t = C_1 \ln \frac{n}{n(0)} + \frac{C_2}{n} \left[ 1 - \frac{n}{n(0)} \right] \quad (3)$$

where  $C_1 = (\beta - \alpha)/\gamma\alpha$  and  $C_2 = \beta N/\gamma\alpha$ .

The curves for decay at  $0^\circ$  and  $30^\circ \text{C}$  shown in figure 3 (p. 4) are equation (3) fitted to the experimental data. It is important to note that while the loss of  $V_1$  centers correlates quite well with the catalytic activity, there is a possibility that the E levels are the active sites. Wertz and coworkers (ref. 12) have shown that the formation and decay of  $\text{Fe}^{+1}$  ions in single crystals are similar to those of the  $V_1$  center. They, along with others, (refs. 11 and 13), have suggested that these ions might be the filled E levels. The  $\text{Fe}^{+1}$  ion spectrum has also been observed by the author in single crystals at  $4^\circ \text{K}$  following ultraviolet irradiation, but the spectrum has not been found in powder samples that show the  $V_1$  spectrum.

The problem is then to decide whether a  $V_1$ -type center is the irradiation-induced active site for catalysis or whether it is related only in an indirect manner. The fact that the  $V_1$  center interacted quite strongly with  $\text{H}_2$  in the P-3 sample indicates an affinity of the center for  $\text{H}_2$ . It is recognized, of course, that the formation of very strong bonds between the reaction products and the adsorbent is not conducive to high catalytic activity. Perhaps, because of structural differences, the bonds between P-1 and  $\text{H}_2$  were weaker than the bonds between P-3 and  $\text{H}_2$  and the equilibrium reaction





was shifted to the left so that the change in the number of  $V_1$ -type centers was not detected upon exposure of P-1 to the reactants. This possibility is tantamount to saying that  $HV_1$  is a reaction intermediate of low concentration.

In a more general sense, this work confirms that the enhanced catalytic activity is directly related to an electronic phenomenon. This proposition has been set forth by several investigators for insulator-type catalysts (refs. 14 to 16). Furthermore, in the light of the results of this report it is difficult to support an alternative mechanism which supposes that irradiation simply moves hydroxyl groups from active sites to inactive sites and that at some later time these poisons diffuse back. It is possible that hydroxyl groups at the surface act as the primary electron traps and that these are the active sites. Such centers would be expected to show an electron paramagnetic resonance signal that could be correlated with the enhanced activity, but no such signal was observed in samples degassed at  $290^\circ\text{C}$ .

### CONCLUSIONS

From a study of irradiation-induced active sites on magnesium oxide with the use of electron paramagnetic resonance, the following conclusions were drawn:

1. The experimental data show that a correlation exists between the ultraviolet irradiation enhanced catalytic activity and the  $V_1$  center concentration. (The  $V_1$  center is defined as a hole trapped at an anion adjacent to a cation vacancy.)
2. This correlation strongly suggests that either a  $V_1$ -type center existing on the surface is an active site for the hydrogen-deuterium exchange reaction or the  $V_1$  center formation is an integral step in the formation of the active site; that is, it is a hole trap that prevents recombination.

Lewis Research Center

National Aeronautics and Space Administration  
Cleveland, Ohio, June 5, 1964

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